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New Directions towards the Understanding of Physico-Chemical Processes in Aquatic Systems

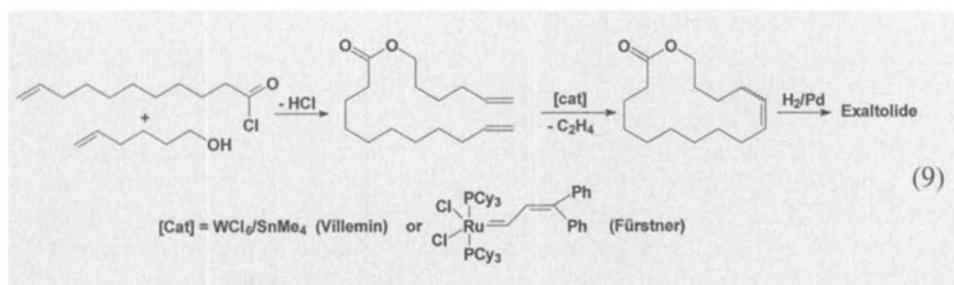Christine Couture, Charles-Philippe Lienemann, Denis Mavrocordatos, and Didier Perret*

Abstract. Some applications of Analytical Electron Microscopies (AEM) for the characterization of colloids in natural waters are presented. These techniques go much beyond the basic level of morphological observation and render possible to gain detailed physico-chemical information difficult to obtain by conventional analytical methods. Hence, AEM appear as a challenging necessity for understanding the colloid-mediated transport of toxics in the environment.

1. Introduction

Because of the ever increasing demand on water resources, efforts have been directed during the last decades towards water sanitation, and in the development of models for predicting the response of water systems to anthropogenic constraints.

This paper briefly describes our research, which is focused on the microscale characterization of colloids in aquatic systems, and on the understanding of their transformation processes, their reactivity, and their role in the scavenging of toxic trace elements and nutrients.

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New Directions towards the Understanding of Physico-Chemical Processes in Aquatic Systems

Christine Couture, Charles-Philippe Lienemann, Denis Mavrocordatos, and Didier Perret*

Abstract. Some applications of Analytical Electron Microscopies (AEM) for the characterization of colloids in natural waters are presented. These techniques go much beyond the basic level of morphological observation and render possible to gain detailed physico-chemical information difficult to obtain by conventional analytical methods. Hence, AEM appear as a challenging necessity for understanding the colloid-mediated transport of toxics in the environment.

1. Introduction

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2. The Need for Modern Analytical Tools

The description of interactions between aquatic particles and their milieu requires instrumentation capable of recording detailed and subtle modifications in their morphology and chemical composition. Analytical electron microscopies (AEM), which combine scanning (SEM), transmission (TEM), or scanning-transmission (STEM) electron microscopes with energy-dispersive (EDS) or electron-energy loss (EELS) spectrometers, are the optimum tools for this task. AEMs offer high lateral resolution and the possibility of detecting and quantifying virtually every element, at low concentration levels.

Combined efforts in the development of unbiased specimen preparation schemes, labeling organic matter, and accurate TEM-EELS methodologies for environmental samples [1–8] have lead to close-to-routine AEM protocols for the qualitative/quantitative study of aquatic colloids over a large range of sizes (nm to μm) and types (mineral to organic).

3. Soils and Mobility of Colloids

The Arpette valley (VS, CH) is characterized by well developed soils where the transport of major ions and toxic compounds has been extensively studied at the bulk level. Particulate matter within this alpine podzol was isolated from each sharply stratified horizon by means of lysimeters (mobile phase), sequential centrifugations (stationary phase), and whole soil centrifugation (interstitial phase) [2][3]. The mobile colloids, which mediate the transfer of matter within the soils, were then highlighted by AEM.

Micrographs show (*Fig. 1*) that each horizon (O = organic, E = weathering, BP = illuvial, h = humics, s = sesquioxides) exhibits distinct morphological families of particles within a broad size range. Their composition, often revealing mixed aggregates, was determined by AEM on a *per particle* basis. In this case, elemental mapping (TEM-EELS imaging) allowed us to identify the details of these colloids (*Fig. 1b*; nanometer-sized iron oxides in the E horizon) which are often obscured by bulk chemical analyses.

4. Groundwaters and Particles Stability or Transformation

As one of the potential sites for repository of nuclear wastes in Switzerland, the Wellenberg area (LU, CH) is considered with respect to the possibility of radionuclides remobilization. Reduced (Eh = –310 mV) deep groundwater (–360 m; host rock: Valanginian marl) is frequently sampled and exhibits little compositional variation over long periods of time. The particles mainly consist of equal proportions of chlorite, illite, and smectite at low concentrations ($[part]_{max} < 0.5$ mg/l). However, a comparative study (static and dynamic light scattering, SEM and TEM) of this groundwater produced controversial particle-size distributions [9]; this may lead to a biased estimation on the mechanisms of elimination of particles from the aquifer. Indeed, bulk spectrometric measurements of unfractionated samples underestimate small colloids (shadowed by larger particles), while SEM requires special attention for their visualization (limitations in lateral resolution).

On the other hand, TEM measurements of unbiased specimens, allowed identification of colloids as small as 30 nm; an accurate particle-size distribution (*Fig. 2*) was obtained by computerized image analysis of *ca.* 9000 particles. The slope of this distribution ($\beta = 2.2$) indicates that clay colloids are subject to elimination from the Wellenberg groundwater by orthokinetic coagulation.

Another example of the usefulness of AEM is given in the study on the transformation of particulate material within a karstic aquifer in the Ponts valley (NE, CH). Bulk chemical analyses have shown that the concentration of iron dramatically varies from the inlet (Bied brook; *ca.* 740 mg/l) to the outflow (Noiraigue spring; *ca.* 110 mg/l) of the aquifer. These results suggest that Fe-rich particles could undergo physico-chemical transformations (scavenging, ageing) during their transport within the karst [10].

AEM analyses (SEM-EDS; STEM-EDS) revealed that the composition and size of the individual particles (*ca.* 600 entities analyzed) varies from the inlet to the outflow of the aquifer (*Fig. 3, a, b*), the most striking changes being observed for Fe-Ca-Si-rich entities (absent in the Bied; *ca.* 20% of particles in the Noiraigue) and for Fe-Ca-rich entities (*ca.* 50% of particles in the Bied; <10% in the Noiraigue).
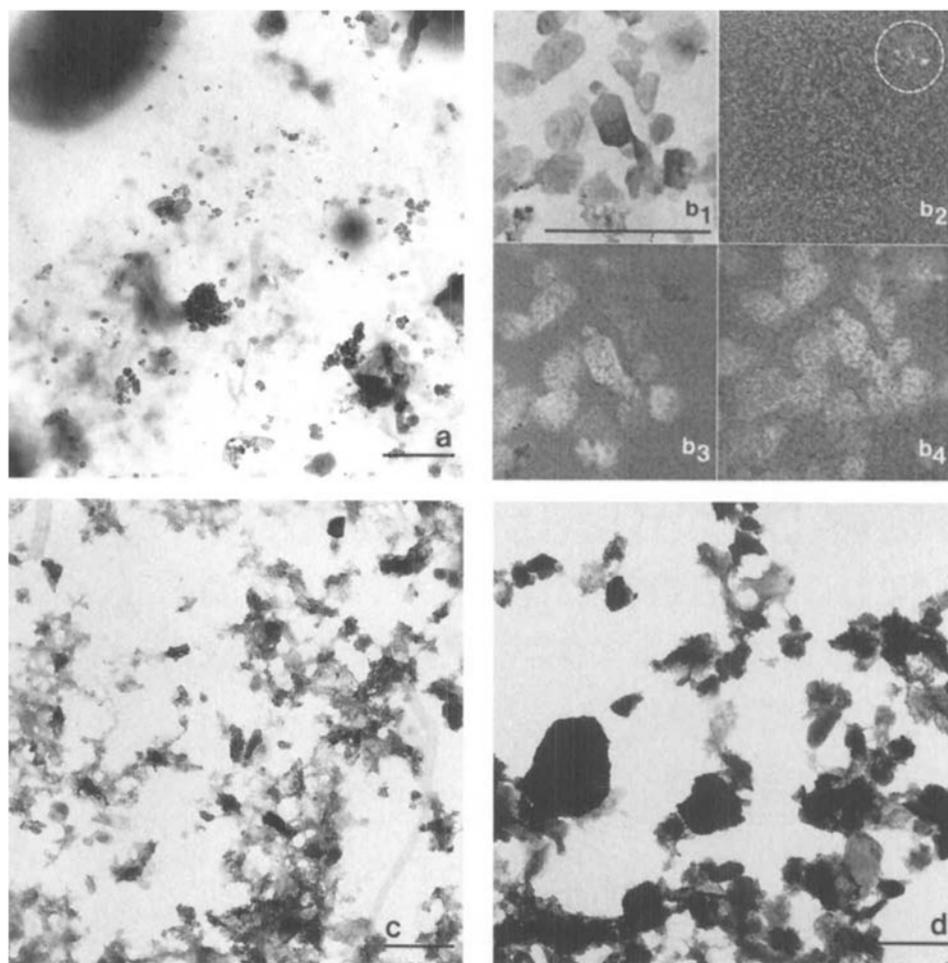

Fig. 1. *Micrographs of soil suspensions from* a) *the O horizon,* b) *the E horizon* (b$_1$: TEM; b$_2$, b$_3$, b$_4$: TEM-EELS imaging of Fe-L$_{2,3}$ edge, Si-K edge, Al-K edge; note the difference in composition between individual colloids), c) *the BP$_h$ horizon, and* d) *the BP$_s$ horizon of the podzol in the Arpette valley.* Scale bars = 0.5 μm.

STEM-EDS imaging of Fe-Ca-rich colloids (*Fig. 3, c*) revealed spectacular quasi-spheres with a yet unidentified core (perhaps humic material) and an ultrathin Si-rich layer acting as inter-colloid cement. Finally, clay particles (Al-Si-rich) in the Bied were shown to contain non-negligible and variable amounts of Fe-Ca-rich entities, suggesting that the latter could exist as individual particles and also as coating of clays.

5. Rivers and Interactions between Organics and Minerals

The nature and sizes of the particulate material present in river waters are highly diverse. They usually reflect the processes of drainage and weathering in the watershed (pedogenic organic matter and mineral particles of soil or rock origins) and the biotic production of aquagenic organic macromolecules (mostly algal and bacterial polysaccharides). In that respect, micrographs from the Rhine River (*Fig. 4, a*) are typical of this heterogeneity. Never-
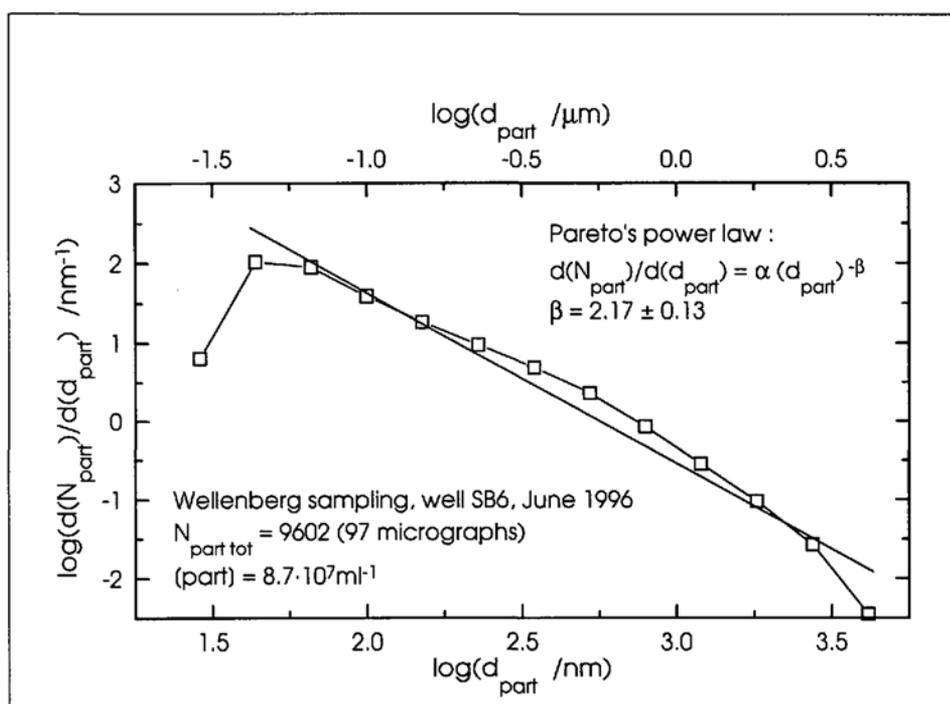

Fig. 2. *Particle-size distribution of clay particles sampled in the Wellenberg groundwater and measured by TEM and image analysis.* The distribution is expressed according to the *Pareto*'s law: $\log(d(N_{part})/d(d_{part})) = f(\log(d_{part}))$, with N_{part} = number of particles in a given size interval and d_{part} = diameter of particles. The slope β of the power law $d(N_{part})/d(d_{part}) = \alpha(d_{part}) - \beta$ is an estimate for the processes of elimination of colloids.
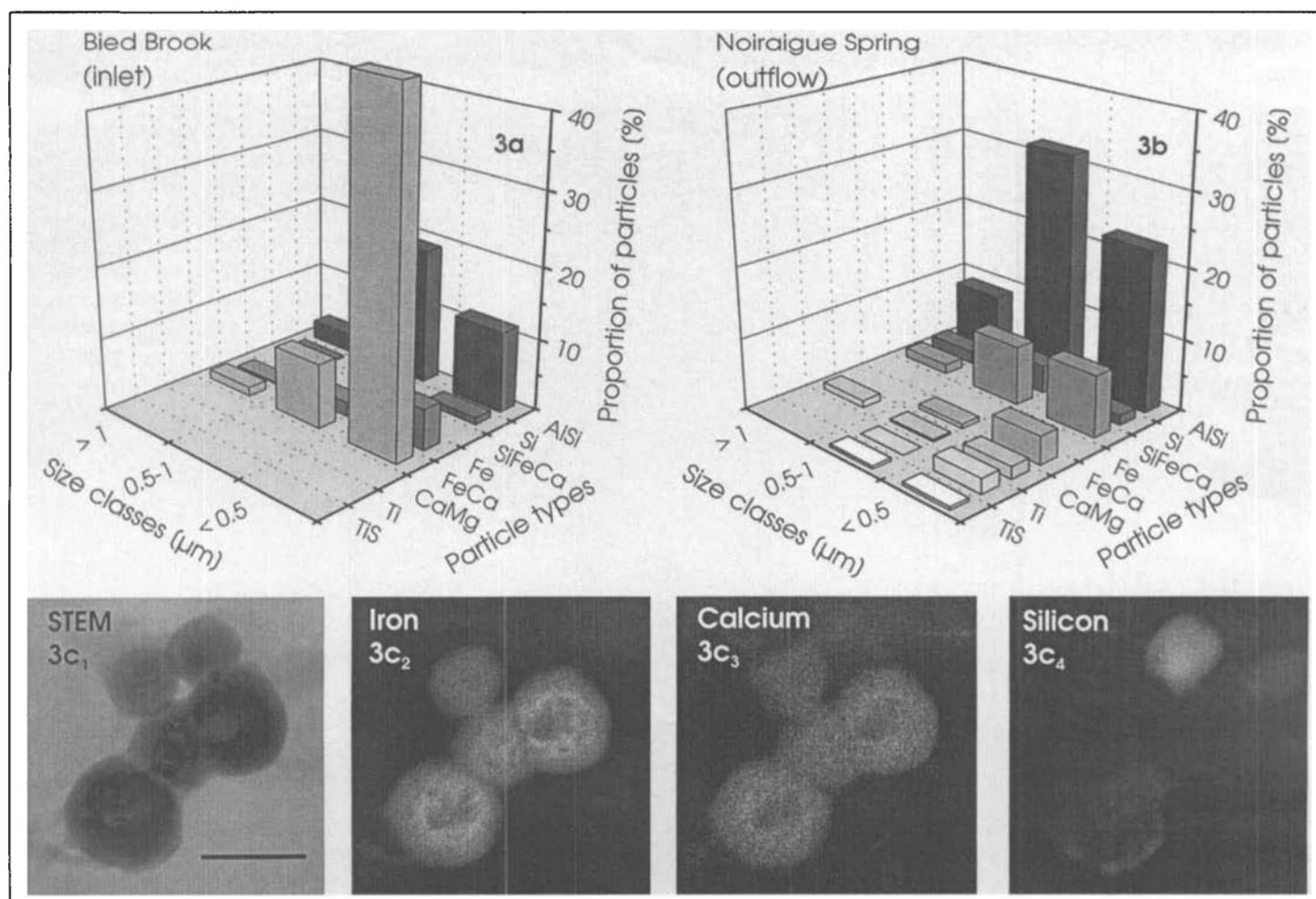

Fig. 3. *Size-ordered composition of particles sampled* a) *in the Bied brook* (inlet of the aquifer), *and* b) *in the Noiraigue spring* (outflow of the aquifer), *and analyzed by STEM-EDS; the labels of particle types express the major elements detected in these particles.* c) *Micrographs of Fe-Ca-rich particles in the Bied brook* (c_1: STEM; c_2, c_3, c_4: STEM-EDS imaging of Fe, Ca, Si). Scale bars = 0.1 µm.

theless, a careful examination of such micrographs reveals that the majority of mineral entities (electron-dense particles) are systematically connected to networks of thin fibrillar bio-material [11]. In the laboratory, attachment of mineral particles to flexible polysaccharide fibrils at low concentrations (*Fig. 4, b*) provides an adequate model for the behavior of such entities in natural waters [4].

To a certain extent, these mineral-organic entities happen to be ubiquitous in natural aquatic systems where bacterial and photosynthetic activity is important (rivers, lakes, oceans). With advanced TEM-EELS imaging [1], it is even possible to detect apparently invisible networks of organic fibrils [7]. The existence of such entities is usually not taken into account. However, although yet poorly understood, the attachement of a mineral particle to a highly hydrated organic macromolecule must influence its physicochemical characteristics: *e.g.*, lowering of the coagulation efficiency due to limited degree of freedom within the network,

modification of the sedimentation rate as a consequence of the change in size and density, variation of the reactivity after deactivation of the surface groups involved in the attachment to organic fibrils.

6. Lakes and Scavenging of Toxics and Nutrients

Lake Lugano (TI, CH; z_{max} = 288 m; S = 27.5 km^2) and Paul Lake (MI, USA; z_{max} = 12 m; S = 10^{-2} km^2) are two typical meromictic lakes with a temporally stable oxic-anoxic interface in their water column. The sharp depth discrimination between their Mn-rich and Fe-rich layers makes these lakes particularly suited for the study of the autochthonous production of manganese oxides (MnO_x) and iron oxihydroxides (FeOOH) and their role in the scavenging of toxic trace elements and nutrients.

Although O_2, Mn_{tot}, and Fe_{tot} profiles in both lakes present similarities (*Fig. 5, a*), their major chemistries are quite differ-

ent (Lugano: PO_{4max} = 0.3 μM, ΣH_2S_{max} = 20 μM, Fe_{max} = 7 μM, Mn_{max} = 5 μM; Paul: PO_{4max} = 10 μM, ΣH_2S_{max} = 20 μM, Fe_{max} = 120 μM, Mn_{max} = 5 μM). Microscopic analyses of Mn-rich and Fe-rich entities isolated from their respective water layers reflect these subtle differences [12][13].

In Lake Lugano, Mn-oxidizing bacteria, with a '*Metallogenium*'-like structure, are covered with sheathed MnO_x having large specific surface area, while in Paul Lake spherical bacteria which oxidize upward-diffusing Mn^{2+} are covered with a thick and compact crust of particulate Mn (*Fig. 5, b*). A careful examination of TEM-EDS spectra (*Fig. 5, d*) indicates that Mn_{part} in Lake Lugano systematically contains phosphorus, iron, silicon, and calcium, with PO_4 and Fe being strongly correlated. In Paul Lake, STEM-EDS analyses on individual particles show that Mn_{part} randomly contains iron, but appears to be a powerful scavenger of cobalt: [Co]:[Mn] in individual Mn_{part} is *ca.* 10 times higher than [Co]:[Mn] inferred from bulk chemical analyses of the water column ($[Co^{2+}]_{max}$ = 10 nM), where profiles of Co and Mn are apparently correlated [12].

Fe-rich colloidal entities in Lake Lugano are usually nano-granules attached onto micrometric networks of fibrils produced by and connected to their parent bacteria, while in Paul Lake, Fe_{part} exists as an intimate mixture of organic-rich fibrillar material and iron, with unusual non-granular morphologies (*Fig. 5, c*). The polysaccharidic nature of the fibrils present in these organo-mineral entities has been unequivocally assigned by applying selective labeling (silver proteinate probe) to carbohydrates on AEM specimens [8]. As opposed to Paul Lake (low $[PO_4]_{tot}$), TEM-EDS spectra (*Fig. 5, e*) show that
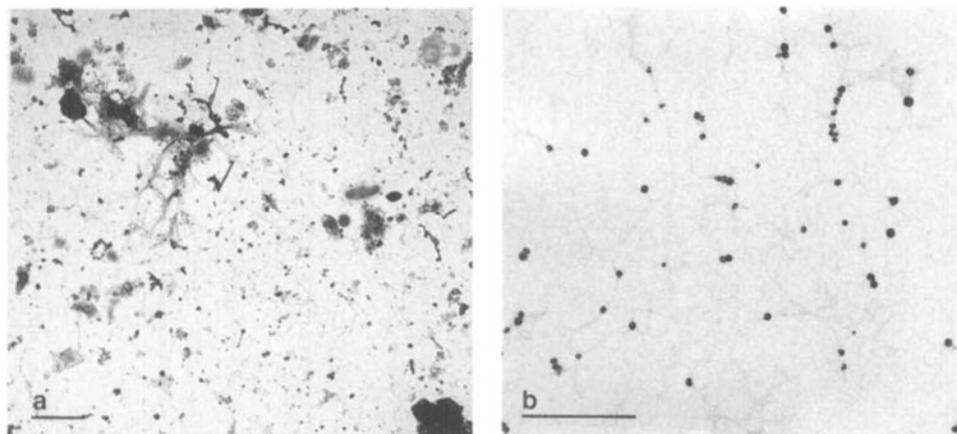

Fig. 4. *Micrographs of* a) *a water sample from the Rhine River,* b) *a model suspension of hematite micro-particles* (α-Fe_2O_3) *and polysaccharide fibrils* (xanthan). Scale bars = 1 μm.
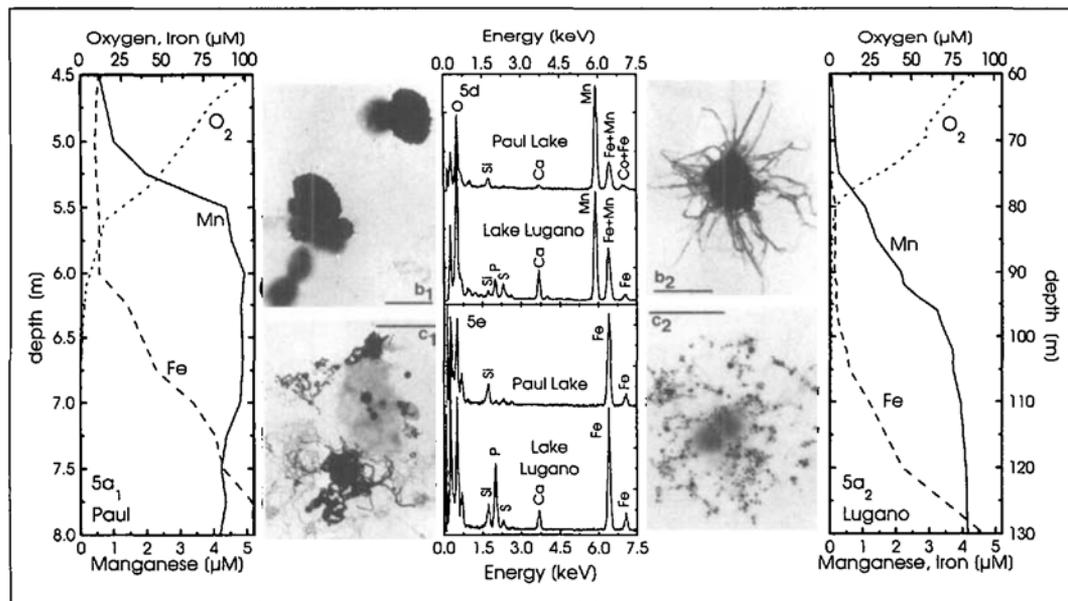

Fig. 5. O_2, Mn_{tot}, Fe_{tot} *profiles in the water columns of* (a_1) *Paul Lake and* (a_2) *Lake Lugano.* Micrographs of (b) Mn-rich particles and (c) Fe-rich particles isolated from Paul Lake (b_1, c_1) and Lake Lugano (b_2, c_2); scale bars = 1 μm. TEM-EDS spectra of (d) Mn-rich particles and (e) Fe-rich particles in Paul Lake (upper spectrum in each box) and Lake Lugano (lower spectrum).

Fe-rich entities in Lake Lugano systematically contain large amounts of phosphorus, the ratio $[PO_4]:[Fe]$ in *ca.* 1000 individual Fe_{part} being higher and more correlated than the ratio extrapolated from bulk chemical analyses. It is thus suggested from microscopic observations that polysaccharides act as nucleation sites for the oxidation of Fe^{2+} into Fe_{part} in both lakes; Fe_{part} in Lake Lugano in turn acts as a strong scavenger of upward-diffusing phosphates, thus probably limiting the auto-eutrophication of this lake [13].

7. Conclusion and Future Prospects

At a first glance, results of the AEM investigations are in agreement with data from more classical bulk chemical analysis schemes. However, AEM allows the accurate description of characteristics or processes at the level of individual particles, and proves unrivalled in extracting chemical associations that are difficult to deduce from the water chemistry or that might simply be incidental.

The continued development and refinement of sophisticated AEM proce-dures in the near future will insure that the fine mechanisms governing the transport of toxic substances through the hydrosphere will be better understood and included in predictive models.

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Fluxional Behaviour of Group 9 Metal Carbonyl Clusters

Raymond Roulet*

Abstract. The site exchange processes of carbonyl ligands in homo- and hetero-metallic dodecacarbonyls of Ir and Rh and their derivatives take place by bridge opening and closing of CO's involving three or four metal atoms, and by rotation of terminal CO's about the apical metal centre. Substitution of Ir by Rh in the basal face of the metal framework slows down the first two processes and accelerates the third one, reflecting a significantly more electropositive character of Ir relative to Rh.

A cluster compound is a polymetallic aggregate containing metal–metal bonds and coordinated molecules. Many of them are stereochemically non-rigid or fluxional. Therefore, the static picture of the compound given by X-ray crystallography needs to be complemented by a dynamic one, usually obtained by NMR spectroscopy, describing the pathways by which movement of coordinated molecules occurs relative to the metallic framework. The possible relationship of the migration of small molecules over clusters to those occurring during the chemisorption of small molecules to a metal surface is an additional incentive for such dynamic studies.

The bulk of the studies on the fluxional behaviour of cluster compounds have dealt with the migration of carbon monoxide over tri- and tetrametallic CO clusters. The first proposal for a pathway of CO scrambling was made by *Cotton* in 1966 [1], and involves bridge opening and closing of the CO ligands to move them around the cluster in concerted steps. This pathway is the so-called merry-go-round process.

The present report presents a detailed picture of the merry-go-round, as well as of other scrambling pathways found to take place in homo- and heterometallic dodecacarbonyls of Ir and Rh and their derivatives.

1. The Merry-go-round

1.1. *Clusters of* C_{3v} *Symmetry*

The ground-state geometry of $Rh_4(CO)_{12}$ in solution has C_{3v} symmetry [2]. A simulation of its variable-temperature and -pressure ^{13}C-NMR spectra [3] (*Fig. 1, a*) has shown that the fluxional process leading to complete CO scram-

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